

## PATENT ABSTRACTS OF JAPAN

(11)Publication number : 2001-015173

(43)Date of publication of application : 19.01.2001

(51)Int.Cl.

H01M 10/40

H01M 4/58

(21)Application number : 2000-131537

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(22)Date of filing : 26.04.2000

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(30)Priority

Priority number : 11119537

Priority date : 27.04.1999

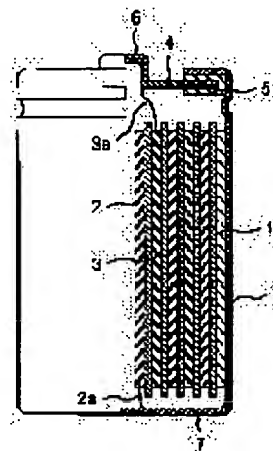
Priority country : JP

## (54) LITHIUM SECONDARY BATTERY

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a battery having a long service life under high temperature, capable of responding to fluctuation in power supply or load, and quickly receiving and feeding the power, by using a material including specific amorphous carbon for a negative material, using specific spinel type crystal structure for a positive electrode, and forming it of a specific composite oxide including Li and Mn.

SOLUTION: This lithium secondary battery is so formed that an active material of a negative material includes amorphous carbon, its negative electrode density is larger than 0.95 g/cm<sup>3</sup> and smaller than 1.5 g/cm<sup>3</sup>, an active material of the positive electrode has the half width of 2θ angle of the (400) peak of X-ray diffraction



pattern smaller than  $0.2^\circ$ , the positive electrode includes composite oxide including Li and Mn having a spinel type crystal structure, Li/Mn atom ratio of the composite oxide is larger than 0.55 and smaller than 0.8, the lattice constant in the spinel type crystal structure is larger than  $8.031 \text{ \AA}$  and smaller than  $8.23 \text{ \AA}$ , the specific surface of secondary particles of the composite oxide is larger  $0.1 \text{ m}^2/\text{g}$  and smaller than  $1.5 \text{ m}^2/\text{g}$ , and the mean grain size of the primary particles of the composite oxide is larger than  $1 \text{ }\mu\text{m}$  and smaller than  $20 \text{ }\mu\text{m}$ .

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## LEGAL STATUS

[Date of request for examination] 14.11.2002

[Date of sending the examiner's decision of rejection]

[Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]

[Date of final disposal for application]

[Patent number]

[Date of registration]

[Number of appeal against examiner's decision of rejection]

[Date of requesting appeal against examiner's decision of rejection]

[Date of extinction of right]

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## DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[The technical field to which invention belongs] This invention relates to a lithium secondary battery.

[0002]

[Description of the Prior Art] Since cell voltage is high energy density highly, development is prosperous in the lithium secondary battery using nonaqueous electrolyte, and utilization has already progressed as objects for information machines and equipment, such as a computer and a cellular phone.

[0003] However, by the high input, high power, and the mass industrial cell, since a lot of active materials are needed, with Co system and nickel system material which are used for information machines and equipment, utilization is made impossible from a cost side and both sides of the amount of resources. For this reason, the spinel mold Mn system material is expected as what solves these troubles. However, with a spinel mold Mn system material, there was a problem which said that the cycle life in the elevated temperature which is the problem of the utmost importance of an industrial cell, and output characteristics and input characteristics were bad.

[0004] Although the life of 1000 or more (70% or more of capacity maintenance factors) cycles and the output of 500 or more W/kg were needed at the elevated temperature 50 degrees C or more in order to apply a lithium secondary battery to power supplies, such as an electric vehicle, a parallel hybrid electric vehicle, a stationary-energy-storage system, and an elevator, a power tool, with the conventional Mn system material, such reinforcement and high-power-density-izing were impossible.

[0005] According to JP,6-187993,A, reinforcement is tried by enlarging the Li/Mn ratio which is a presentation ratio of Li and Mn. However, about several% of capacity fall has taken place by passing through the charge and discharge of 10 cycles also at a room temperature. the cycle life of a lithium secondary battery is greatly influenced to a surrounding temperature -- having -- especially -- an elevated temperature 50 degrees C or more -- a room temperature -- a life -- remarkable -- short -- it keeps that it is \*\*\*\*\*. Therefore, it is difficult to acquire the cycle life of 1000 or more cycles at an elevated temperature 50 degrees C or more only by enlarging a Li/Mn ratio.

[0006] Moreover, JP,8-24043,B enlarged the Li/Mn ratio similarly, calcinated this at 430-510 degrees C, and the lattice constant has tried this for it with the material 8.22A or less. However, there is no prospect that the cycle life of 1000 or more cycles is acquired above a 200 cycle degree and 50 degrees C also at a room temperature. Moreover, although reinforcement is in drawing in JP,7-282798,A using  $\text{Li}(\text{Mn}_{2-x}\text{Li}_x)\text{O}_4$  ( $0.020 \leq x \leq 0.081$ ) which is the large material of a Li/Mn ratio too, if 100 cycle degree progress is carried out at a room temperature even when referred to as  $x = 0.081$  (Li/Mn=0.58), 5% of capacity fall arises and the cycle life of 1000 or more cycles cannot be acquired at an elevated temperature 50 degrees C or more.

[0007]

[Problem(s) to be Solved by the Invention] As a short cause of such a life, each is because a repeat, consequently a crystal collapse and reversible occlusion emission of a lithium becomes impossible

[ expansion contraction ] also as for positive active material by repetition of the charge and discharge of multiple times. And under an elevated temperature, it is for Mn ion to begin to melt into the electrolytic solution, and for the crystal of positive active material further to become easy to collapse rather than a room temperature. Moreover, Mn ion which began to melt deposits in a negative electrode, checks the charge-and-discharge reaction of a negative electrode, and shortens the life of a negative electrode.

[0008] Moreover, since ionic conductivity uses the low organic solvent compared with the aqueous solution system as the electrolytic solution, the cause that the output characteristics of a lithium secondary battery and input characteristics are low is because the diffusion rate concerning insertion and emission of a lithium ion is low. Especially, on the negative-electrode surface, the lithium ion which it becomes impossible to have not been unable to react and separated reacts with an organic solvent, a coat is formed, the diffusion rate of a lithium ion falls further by resistance of this coat, and output characteristics and input characteristics worsen. Moreover, since, as for the organic solvent which is the electrolytic solution, the ionic conductivity in low temperature falls remarkably, the output characteristics at the time of low temperature and input characteristics get still worse.

[0009] The 1st purpose of this invention is in the thing to depend on solving these troubles and using a long lasting material under an elevated temperature and power receiving or the lithium secondary battery which can be supplied is promptly offered [ a thing ] for power corresponding to fluctuation of a power supply or a load as it is long lasting.

[0010] The 2nd purpose of this invention is to offer the lithium secondary battery which was excellent in the property as objects for power supplies, such as an electric vehicle, a parallel hybrid electric vehicle, a stationary-energy-storage system, an elevator, and a power tool.

[0011]

[Means for Solving the Problem] It is characterized by a lithium secondary battery of this invention consisting of a multiple oxide which has the ~~spinel~~ mold crystal structure and contains Li and Mn as a positive electrode using a material which contains amorphous carbon as a negative electrode.

[0012] Although a multiple oxide uses Li and Mn as an essential element as a positive electrode of this invention, an element of other transition metals except Mn, an Ila group, or an IIIb group may also be included. As such a thing, they are Ti, V, Cr, Fe, Co, nickel, Cu, Zn, Be, Mg, calcium, Sr, Ba, Ra, B, aluminum, Ga, In, Tl, etc., for example.

[0013]

[Embodiment of the Invention] First, the configuration of a positive electrode and a negative electrode is explained.

[0014] As positive active material of this invention, the Li/Mn atomic ratio of a multiple oxide uses what is smaller than 0.80 larger than 0.55. if a Li/Mn atomic ratio repeats a charge-and-discharge cycle above 50 degrees C 0.55 or less -- Mn ion -- the inside of the electrolytic solution -- dissolving -- the crystal structure -- collapsing -- a cycle life -- short -- \*\*\*\* -- \*\* Moreover, discharge capacity becomes [ a Li/Mn atomic ratio ] small or more by 0.80.

[0015] Smaller [  $A / 8.031$  ] than 8.230Å, the lattice constant in the spinel mold crystal of the multiple oxide of this invention comes size, and is characterized by things. When a lattice constant repeats a charge-and-discharge cycle above 50 degrees C by 8.230Å or more, Mn ion dissolves into the electrolytic solution, the crystal structure collapses, and a cycle life is short. Moreover, a lattice constant is \*\* with a small discharge capacity at 8.031Å or less.

[0016] Furthermore, the multiple oxide of this invention is characterized by the half-value width of 2theta angles of the peak (400) of an X diffraction pattern being smaller than 0.20 degrees. The thing of the slit width of  $DS=SS=0.5$  and  $RS=0.15$  was used for measurement of an X diffraction as a slit, using Cu-k alpha rays as a line source. If half-value width repeats a charge-and-discharge cycle above 50 degrees C at 0.20 degrees or more, Mn ion will dissolve into the electrolytic solution, the crystal structure will collapse, and a cycle life will become short.

[0017] Moreover, specific surface area of the secondary particle of the multiple oxide of this invention is characterized by being smaller [ than  $1.5\text{m}^2/\text{g}$  ] larger than  $0.10\text{m}^2/\text{g}$ . When specific surface area repeats a charge-and-discharge cycle above 50 degrees C above  $1.5\text{m}^2/\text{g}$ , Mn ion dissolves into the electrolytic

solution, the crystal structure collapses, and a cycle life is short. Moreover, below by  $0.10\text{m}^2/\text{g}$ , in rapid charge and discharge, since the own reaction field of an electrode active material is small, power efficiency becomes [ specific surface area ] low.

[0018] It is characterized by the mean particle diameter of the primary particle of the multiple oxide of this invention being still larger than 1 micrometer, and being smaller than 20 micrometers. When mean particle diameter repeats a charge-and-discharge cycle above 50 degrees C by 1 micrometer or less, Mn ion dissolves into the electrolytic solution, the crystal structure collapses, and a cycle life is short.

Moreover, by 20 micrometers or more, in boosting charge or rapid discharge, since the own reaction field of an electrode active material is small, power efficiency becomes [ mean particle diameter ] low.

[0019] The positive electrode of this invention has a long life in an elevated temperature for the first time by combining with the negative electrode containing amorphous carbon, and the target lithium secondary battery is obtained. Furthermore, it is characterized by negative-electrode density being more greatly [ than  $0.95\text{ g/cm}^3$  ] smaller than  $1.5\text{ g/cm}^3$  at the negative-electrode active material of the lithium secondary battery of this invention, including amorphous carbon.

[0020] If a charge-and-discharge cycle is repeated above 50 degrees C, it deposits into the portion which Mn ion dissolves into the electrolytic solution from positive active material, and becomes the deposit onset potential of Mn ion, i.e., the potential not more than 2V. A negative electrode, a separator and a current collection foil, a cell can, etc. serve as a deposit part. The opening of a negative electrode has much negative-electrode density in three or less  $0.95\text{ g/cm}^3$ , and since the specific surface area as an electrode is also large, Mn ion deposits so much in the negative-electrode surface and the interior. Mn which deposited has a short cycle life in order to reduce the capacity of a negative electrode greatly. Since there are few opening portions of a negative electrode in three or more  $1.5\text{ g/cm}^3$ , the electrolytic solution does not permeate [ negative-electrode density ] the interior of an electrode, but negative-electrode capacity becomes low.

[0021] Furthermore, it is characterized by the true density being  $1.2 - 1.8\text{ g/cm}^3$  at the negative-electrode active material of the lithium secondary battery of this invention including amorphous carbon. If a charge-and-discharge cycle is repeated above 50 degrees C, the portion which Mn ion dissolves into the electrolytic solution from positive active material, and becomes the deposit onset potential of Mn ion, i.e., the potential not more than 2V, for example, a negative electrode and a separator, a current collection foil, a cell can, etc. will serve as a deposit part.

[0022] If carbonaceous true density is smaller than  $1.2\text{ g/cm}^3$ , there are many openings inside carbon, and since specific surface area is also large, Mn ion deposits so much in the carbon surface and the interior. in order that Mn which deposited may reduce the capacity of a negative electrode greatly -- a cycle life -- short -- \*\*\*\* -- \*\* Moreover, if carbonaceous true density is larger than  $1.8\text{ g/cm}^3$ , since there are few opening portions of a negative electrode, the electrolytic solution will not permeate the interior of an electrode, but negative-electrode capacity will become low, and it will be hard coming to obtain the target lithium secondary battery.

[0023] Furthermore, it is characterized by the crystal thickness  $L_c$  being 5-150A at the negative-electrode active material of the lithium secondary battery of this invention including amorphous carbon. The carbonaceous crystal thickness  $L_c$  is one of the indexes showing carbonaceous crystallinity, and it is shown that amorphous-izing is strong when  $L_c$  is small, and graphitization is strong if  $L_c$  is large.

[0024] Moreover,  $L_c$  is also the index with which the number of laminatings of a perpendicular direction is expressed to a six membered ring mesh side. It means that there are few laminatings when  $L_c$  is small, and there is it, still few six membered ring ends, i.e., insertion / emission site of a lithium, and if  $L_c$  is large, it means that there are many laminatings and there are, a six membered ring end, i.e., insertion / emission site of a lithium. [ many ]

[0025] Since insertion / emission site of a lithium will not be secured if the carbonaceous crystal thickness  $L_c$  is smaller than 5A, insertion and release reaction do not progress smoothly, but the trap of the lithium ion will be carried out strongly in carbon, and output characteristics and input characteristics decline sharply. Moreover, since the property like [ property / like an amorphous substance ] a graphite will become strong if the carbonaceous crystal thickness  $L_c$  is larger than 150A, a six membered ring

mesh side will be piled up in parallel, and a six membered ring end will concentrate on an one direction. Therefore, directivity will be produced to insertion / emission site of a lithium, insertion and emission of a lithium will go only in an one direction to it, and output characteristics and input characteristics fall to it sharply.

[0026] The lithium secondary battery of this invention can obtain the input density of 300 - 1800 W/kg with a cell. Moreover, the power density of 500 - 3500 W/kg is able to obtain with a cell, and it is desirable to use it in this range.

[0027] Furthermore, the lithium secondary battery of this invention can be used as a group cell, and the input density of 200 - 1300 W/kg is obtained. It is desirable to be able to obtain the power density of 360 - 2520 W/kg by this group cell, and to use it in this range.

[0028] As for the lithium secondary battery of this invention, in -10 degrees C - 50 degrees C, the input density of 200 - 1300 W/kg is obtained for service temperature by 300 - 1800 W/kg and the group cell with a cell.

[0029] Furthermore, in -10 degrees C - 50 degrees C, 500 - 3500 W/kg can be obtained with a cell, and, as for the lithium secondary battery of this invention, service temperature can obtain the input density of 360 - 2520 W/kg by the group cell.

[0030] As a method of producing the positive active material of this invention, after mixing a manganese dioxide and a lithium carbonate at a predetermined rate, it is good to perform preliminary baking at the temperature of 500-650 degrees C in air, to calcinate at 800-875 degrees C in air after that for 20 hours or more, and to cool at a speed later than a part for 2-degree-C/. Thus, grain growth also has highly remarkable crystallinity and the produced positive active material shows a long lasting cycle property good also under an elevated temperature.

[0031] Especially, the cycle life of 1000 or more cycles is acquired, and even an elevated temperature 50 degrees C or more has high input characteristics and output characteristics in the temperature requirement which is -10 degrees C - 50 degrees C. Therefore, power assistance can apply to a required power supply etc.

[0032] In order to extend the charge-and-discharge cycle life in an elevated temperature, it is important to raise the stability of the crystal of positive active material and to control decay of the crystal structure accompanying a charge-and-discharge reaction.

[0033] It is the chemical decay to which there are two factors in decay of the crystal structure accompanying a charge-and-discharge reaction, one is mechanical destruction caused by expansion contraction of the grid at the time of charge and discharge, and tetravalent Mn which produces another at the time of charge is caused by forming the organic solvent and the organic complex in the electrolytic solution, and being eluted out of crystal system.

[0034] Since the large material of a Li/Mn ratio is used for the positive active material of this invention, compared with Mn<sup>3+</sup> ion, the rate of Mn<sup>4+</sup> ion with a small ionic radius can increase relatively, and it can reduce grid distortion by suppressing the Jahn-Teller instability of Mn<sup>3+</sup> ion, and can control mechanical decay and chemical decay.

[0035] for example, at the time of Li/Mn=0.50, the chemical composition type of LiMn 2O4 is followed -- if it becomes and will think from charge neutrality -- the average valence of Mn ion -- 3.5 \*\*, i.e., Mn<sup>3+</sup>, and Mn<sup>4+</sup> -- \*\* -- it becomes a number of thing. When it calculates from the empirical formula of Li<sub>1+x</sub>Mn<sub>2-x</sub>O<sub>4</sub> at the time of Li/Mn=0.58, the average valence of Mn ion is set to +3.63, and the rate of tetravalent Mn<sup>4+</sup> ion will increase it relatively.

[0036] At this time, a lattice constant is small compared with the case of the former, therefore since the amount of expansion contraction in the case of charge and discharge decreases, it can control mechanical decay. Moreover, since the part and the lithium which cannot be emitted remain in crystal system if the valence of Mn approaches tetravalence, it becomes a stanchion supporting the crystal structure, and works, and mechanical decay and chemical decay can be controlled.

[0037] Moreover, crystallinity is high, since grain growth is also remarkable, its stability of a crystal is remarkable, and the positive active material of this invention can control mechanical decay and chemical decay.

[0038] However, even if it uses the positive active material of this invention and does not result by chemical decay depending on the temperature conditions of charge and discharge, the elution of a certain amount of Mn is not avoided. It is to become a problem when Mn is eluted, or eluted Mn deposits where, if Elution Mn deposits in a negative electrode preferentially, negative-electrode capacity will fall and a cycle life will become short. By making high density of a negative electrode, or carbonaceous true density, for controlling this, the deposit part to a negative electrode can be reduced and a capacity fall can be controlled.

[0039] Moreover, in order to obtain a long lasting industrial cell, what surely contains amorphous carbon as a negative electrode is used. Since the cycle life is short when the negative electrode which does not contain amorphous carbon is used, as an industrial cell for which even an elevated temperature 50 degrees C or more needs the cycle life of 1000 or more cycles, it is not desirable.

[0040] When carbon negative electrodes other than conventional amorphous carbon are used, above 50 degrees C, it is easy to disassemble the organic solvent currently used as the electrolytic solution, and it tends to form carbon dioxide gas, a hydrocarbon or a lithium alkoxide, etc. Compared with other carbon materials, since there is comparatively little disassembly of such the electrolytic solution, amorphous carbon can attain reinforcement in an elevated temperature.

[0041] Moreover, in order to raise output characteristics and input characteristics to the carbon material which forms a cell, it is good for it to use the carbon material which is always in the optimal range of the crystal thickness  $L_c$ . Even if  $L_c$  is too large, output characteristics and input characteristics are affected - even if too small, the number of insertion / emission sites of a lithium decreases, or directivity arises and insertion / emission speed falls.

[0042] The lithium secondary battery which has high input characteristics and output characteristics for the first time is obtained by combining the positive electrode and negative electrode of this invention. Furthermore, even when the cell of this invention is used as a group cell, high input characteristics and output characteristics are obtained.

[0043] By the above, the CHIUMU rechargeable battery with which high input characteristics and output characteristics can apply even elevated temperatures of 50 degrees C or more, such as an electric vehicle, a parallel hybrid electric vehicle, a stationary-energy-storage system, an elevator, and a power tool, or the cycle life of 1000 or more cycles, and a -10 degrees C - 50 degrees C temperature requirement as a required industrial cell can be obtained.

[0044] [Example 1] The mixture which mixed the graphite for polyvinylidene fluoride as a binder 90% of the weight, and mixed 6 % of the weight for positive active material as an electric conduction agent 4% of the weight was applied to the positive electrode to both sides of aluminium foil with a thickness of 20 micrometers after 30-minute \*\*\*\* with the stone milling machine.

[0045] Amorphous carbon powder was used for the negative electrode, and the mixture which mixed polyvinylidene fluoride for acetylene black as an electric conduction agent 87% of the weight, and mixed 7 % of the weight for this as a binder 6% of the weight was applied to both sides of copper foil with a thickness of 10 micrometers after 30-minute \*\*\*\* with the stone milling machine.

[0046] After the above-mentioned positive/negative two poles carried out rolling molding with the press machine and carried out spot welding of the terminal, the vacuum drying of them was carried out at 150 degrees C for 5 hours.

[0047] The laminating of a positive electrode and the negative electrode was carried out through the separator made from fine porosity polypropylene, this was wound spirally, and it inserted in the cell can made from SUS. The negative-electrode terminal was welded to the cell can, and the positive-electrode terminal was welded to the cell lid, respectively. What dissolved one-mol  $\text{LiPF}_6$  in the mixed solution of 11. ethylene carbonate and diethyl carbonate at the electrolytic solution was poured in in the cell can, and the cylindrical cell of 800mAh capacity was produced for the cell lid in total. The cell repeated the cycle which discharges to 2.8V by 800mA by 800mA with the ambient temperature of 50 degrees C after the constant current constant-potential charge of 4.2 V or 7 hours.

[0048] The cycle life and discharge capacity to the Li/Mn ratio of positive active material are shown in drawing 1. In addition, it was made to become about other conditions optimal within the limits which

this invention specifies. The Li/Mn ratio showed the property also with a good cycle-life and discharge capacity in the larger range smaller than 0.8 than 0.55.

[0049] Furthermore, in the cell, in the range whose temperature is -10 degrees C - 50 degrees C, and the range whose depth of discharge is 30 - 80%, input density was in the range of 300-1800W/kg, and power density was in the range of 500 - 3500 W/kg.

[0050] Moreover, in the case of the group cell which connected 96 to the serial for this cell, in the range whose temperature is -10 degrees C - 50 degrees C, and the range whose depth of discharge is 30 - 80%, input density was in the range of 200 - 1300 W/kg, and power density was in the range of 360 - 2520 W/kg.

[0051] [Example 2] The cell was produced like the example 1. Positive-active-material powder was measured by the X diffraction, and it asked for the lattice constant of a spinel mold cubic using the least square method. About other conditions, it considered as optimal within the limits which this invention specifies. The relation of the cycle life over the lattice constant of positive active material and discharge capacity is shown in drawing 2 . The lattice constant showed the property also with a good cycle-life and discharge capacity in the larger range smaller than 8.230Å than 8.031Å from drawing.

[0052] Furthermore, in the cell, in the range whose temperature is -10 degrees C - 50 degrees C, and the range whose depth of discharge is 30 - 80%, input density was in the range of 300-1800W/kg, and power density was in the range of 500 - 3500 W/kg.

[0053] Moreover, in the case of the group cell which connected 96 to the serial for this cell, in the range whose temperature is -10 degrees C - 50 degrees C, and the range whose depth of discharge is 30 - 80%, input density was in the range of 200 - 1300 W/kg, and power density was in the range of 360 - 2520 W/kg.

[0054] [Example 3] The cell was produced like the example 1. (400) The full width at half maximum asked positive-active-material powder for slit width as  $DS=SS=0.5$  and  $RS=0.15$  using the source of CuK alpha rays according to the X diffraction. About other conditions, it considered as optimal within the limits which this invention specifies. The relation between the full width at half maximum (400) of positive active material and a cycle life is shown in drawing 3 . The cycle life of the full width at half maximum (400) was better than drawing in the range smaller than 0.2 (deg.).

[0055] Furthermore, in the cell, in the range whose temperature is -10 degrees C - 50 degrees C, and the range whose depth of discharge is 30 - 80%, input density was in the range of 300-1800W/kg, and power density was in the range of 500 - 3500 W/kg.

[0056] Moreover, in the case of the group cell which connected 96 of this cell to the serial, in the range whose temperature is -10 degrees C - 50 degrees C, and the range whose depth of discharge is 30 - 80%, input density was in the range of 200 - 1300 W/kg, and power density was in the range of 360 - 2520 W/kg.

[0057] [Example 4] The cell was produced like the example 1. About other conditions, it considered as optimal within the limits which this invention specifies. Moreover, it considered as the ratio of the discharge capacity to the charge capacity when discharging to 2.8V by 800mA with the ambient temperature of 20 degrees C about rapid discharge effectiveness at 1600mA after the constant current constant-potential charge of 4.2 V or 7 hours.

[0058] Relation with the cycle life and rapid discharge effectiveness over the specific surface area of the aggregated particle of positive active material is shown in drawing 4 . Specific surface area showed the property also with good cycle-life and rapid discharge effectiveness from drawing in the range larger [than 0.1m<sup>2</sup>/g] and smaller than 1.5m<sup>2</sup>/g.

[0059] Furthermore, in the cell, in the range whose temperature is -10 degrees C - 50 degrees C, and the range whose depth of discharge is 30 - 80%, input density was in the range of 300-1800W/kg, and power density was in the range of 500 - 3500 W/kg.

[0060] Moreover, in the case of the group cell which connected 96 of this cell to the serial, in the range whose temperature is -10 degrees C - 50 degrees C, and the range whose depth of discharge is 30 - 80%, input density was in the range of 200 - 1300 W/kg, and power density was in the range of 360 - 2520 W/kg.



[0061] [Example 5] The cell was produced like examples 1 and 4. About other conditions, it considered as optimal within the limits which this invention specifies.

[0062] Relation with the cycle life and rapid discharge effectiveness over the first [ an average of ] particle diameter of positive active material is shown in drawing 5 . The first [ an average of ] particle diameter showed the property also with good cycle-life and rapid discharge effectiveness in the larger range smaller than 20 micrometers than 1 micrometer from drawing.

[0063] Furthermore, in the cell, in the range whose temperature is -10 degrees C - 50 degrees C, and the range whose depth of discharge is 30 - 80%, input density was in the range of 300-1800W/kg, and power density was in the range of 500 - 3500 W/kg.

[0064] Moreover, in the case of the group cell which connected 96 of this cell to the serial, in the range whose temperature is -10 degrees C - 50 degrees C, and the range whose depth of discharge is 30 - 80%, input density was in the range of 200 - 1300 W/kg, and power density was in the range of 360 - 2520 W/kg.

[0065] [Example 6] The cell was produced like the example 1. About other conditions, it considered as optimal within the limits which this invention specifies. About negative-electrode discharge capacity, the capacity of a negative-electrode single electrode was evaluated by making Li metal into a counter electrode.

[0066] Relation with the cycle life and negative-electrode discharge capacity to negative-electrode density is shown in drawing 6 . Negative-electrode density showed the property also with a good cycle-life and negative-electrode discharge capacity from drawing in the range larger [ than 0.95 g/cm<sup>3</sup> ] and smaller than 1.5 g/cm<sup>3</sup>.

[0067] Furthermore, in the cell, in the range whose temperature is -10 degrees C - 50 degrees C, and the range whose depth of discharge is 30 - 80%, input density was in the range of 300-1800W/kg, and power density was in the range of 500 - 3500 W/kg.

[0068] Moreover, in the case of the group cell which connected 96 of this cell to the serial, in the range whose temperature is -10 degrees C - 50 degrees C, and the range whose depth of discharge is 30 - 80%, input density was in the range of 200 - 1300 W/kg, and power density was in the range of 360 - 2520 W/kg.

[0069] [Example 7] The synthetic method of the positive-electrode material of this invention is explained. As a raw material, electrolytic manganese dioxide and a lithium carbonate were blended so that a Li/Mn ratio might be set to 0.62. Temporary baking of this was carried out at 615 degrees C for 15 hours, and after mixing again, baking of 30 hours was performed at 825 degrees C. A temporary baking production process is an important production process here, in order to raise the homogeneity and the crystallinity of a material and to acquire a good cycle life. Moreover, the cooling rate was considered as a part for 1-degree-C/, and it cooled to the room temperature.

[0070] Thus, when the powder X diffraction of the obtained positive-electrode material was measured using the source of Cuk alpha rays, it checked that it was the crystal structure of a spinel mold without an unusual appearance. The lattice constant at this time was 8.211 Å, and the full width at half maximum (400) was 0.09 degrees. Furthermore, the first [ an average of ] particle size is 3.1 micrometers, and it checked that the specific surface area of an aggregated particle was 0.32m<sup>2</sup>/g.

[0071] Moreover, amorphous carbon was used for the negative electrode and density was made into 1.05 g/cm<sup>3</sup>. The cell was produced like the example 1 and the cycle property in case ambient temperature is 60 degrees C was evaluated. The relation between the number of cycles and discharge capacity is shown in drawing 7 .

[0072] As for this example cell A, the cycle life of 1000 or more cycles was acquired. Furthermore, in the cell, in the range whose temperature is -10 degrees C - 50 degrees C, and the range whose depth of discharge is 30 - 80%, input density was in the range of 300-1800W/kg, and power density was in the range of 500 - 3500 W/kg.

[0073] Moreover, in the case of the group cell which connected 96 of this cell to the serial, in the range whose temperature is -10 degrees C - 50 degrees C, and the range whose depth of discharge is 30 - 80%, input density was in the range of 200 - 1300 W/kg, and power density was in the range of 360 - 2520

W/kg.

[0074] [Example of comparison 1] As a raw material, electrolytic manganese dioxide and a lithium carbonate were blended so that a Li/Mn ratio might be set to 0.62, and baking of 5 hours was performed at 750 degrees C. Moreover, the cooling rate was considered as a part for 5-degree-C/, and it cooled to the room temperature. The lattice constant of the active material obtained at this time is 8.22A, and it turned out that it is within the limits of the lattice constant of this invention. However, the full width at half maximum (400) is 0.4 degrees, and the first [ an average of ] particle size had separated from the specific surface area of 0.6 micrometers and an aggregated particle from the range which is 2.2m<sup>2</sup>/g and this invention pinpoints.

[0075] The cycle property was evaluated having produced the cell for negative-electrode density like the example 1 as 1.05 g/cm<sup>3</sup> of specification within the limits of this invention, and having used surrounding temperature as 60 degrees C. As for this example cell B of a comparison, as for drawing 7 , only the cycle life of a 100 cycle degree showed not being obtained.

[0076] Furthermore, in the cell, input density was the range of 150 - 1300 W/kg in the range whose temperature is -10 degrees C - 50 degrees C, and the range whose depth of discharge is 30 - 80%, and power density was the range of 400 - 2800 W/kg, and was that in which input characteristics and output characteristics are inferior.

[0077] Moreover, in the case of the group cell which connected 96 of this cell to the serial, input density is the range of 90 - 780 W/kg in the range whose temperature is -10 degrees C - 50 degrees C, and the range whose depth of discharge is 30 - 80%, power density is the range of 240 - 1680 W/kg, and it turned out that input characteristics and output characteristics are inferior.

[0078] [Example of comparison 2] As a raw material, electrolytic manganese dioxide and a lithium carbonate were blended so that a Li/Mn ratio might be set to 0.65. Temporary baking of this was carried out at 635 degrees C for 15 hours, and after mixing again, baking of 30 hours was performed at 855 degrees C. Moreover, a cooling rate is a part for 1-degree-C/. At this time, the lattice constant of an active material was 8.190A, and at 0.08 degrees, further, since the first [ an average of ] particle size was 0.12m<sup>2</sup>/g, as for the full width at half maximum (400), the specific surface area of 15 micrometers and an aggregated particle was found [ particle size ] by that the positive active material of this invention is obtained.

[0079] Density is lower than the range of 0.92 g/cm<sup>3</sup> and this invention, concerning a negative electrode on the other hand. The cell was produced like the example 1 and the cycle property in case ambient temperature is 60 degrees C was evaluated. As for this example cell C of a comparison, only the cycle life of 50 cycle degree is acquired from drawing 7 .

[0080] Furthermore, in a cell, in the range whose temperature is -10 degrees C - 50 degrees C, and the range whose depth of discharge is 30 - 80%, input density is the range of 150 - 1300 W/kg, and power density is the range of 400 - 2800 W/kg, and is inferior also in input characteristics and output characteristics.

[0081] Moreover, in the case of the group cell which connected 96 of this cell to the serial, in the range whose temperature is -10 degrees C - 50 degrees C, and the range whose depth of discharge is 30 - 80%, input density is the range of 90-780W/kg, and power density is the range of 240 - 1680 W/kg, and is inferior also in input characteristics and output characteristics.

[0082] [Example of comparison 3] As a raw material, electrolytic manganese dioxide and a lithium carbonate were mixed so that a Li/Mn ratio might be set to 0.51, and baking of 5 hours was performed at 900 degrees C. Moreover, a cooling rate is a part for 1-degree-C/. Although it was out of range, it turned out that the full width at half maximum (400) is [ whose lattice constants at this time are 8.237A and this invention / the specific surface area of 10 micrometers and an aggregated particle of 0.08 degrees and the first / an average of / particle size ] within the limits of 0.15m<sup>2</sup>/g and this invention.

[0083] Moreover, negative-electrode density was made into 1.05 g/cm<sup>3</sup>. The cell was produced like the example 1 and the cycle property in case a surrounding temperature is 60 degrees C was evaluated. As for this example cell D of a comparison of drawing 7 , only the cycle life of a 150 cycle degree is acquired.

[0084] Furthermore, in a cell, in the range whose temperature is -10 degrees C - 50 degrees C, and the range whose depth of discharge is 30 - 80%, input density is the range of 150 - 1300 W/kg, and power density is the range of 400 - 2800 W/kg, and is inferior also in input characteristics and output characteristics.

[0085] Moreover, in the case of the group cell which connected 96 of this cell to the serial, in the range whose temperature is -10 degrees C - 50 degrees C, and the range whose depth of discharge is 30 - 80%, input density is the range of 90-780W/kg, and power density is the range of 240 - 1680 W/kg, and is inferior also in input characteristics and output characteristics.

[0086] [Example of comparison 4] As a raw material, electrolytic manganese dioxide and a lithium carbonate were blended so that a Li/Mn ratio might be set to 0.62, and baking of 5 hours was performed at 850 degrees C. Moreover, a cooling rate is a part for 1-degree-C/. The lattice constant at this time was 8.22A, and the full width at half maximum (400) was 0.1 degrees. Furthermore, the first [ an average of ] particle size is within the limits of this invention by 2 micrometers. However, the specific surface area of an aggregated particle is as large as 1.8m<sup>2</sup>/g.

[0087] Negative-electrode density is 1.05 g/cm<sup>3</sup>. The cell was produced like the example 1 and the cycle property in case a surrounding temperature is 60 degrees C was evaluated. As for this example cell E of a comparison, as for drawing 7 , only the cycle life of a 500 cycle degree showed not being obtained.

[0088] Furthermore, in a cell, in the range whose temperature is -10 degrees C - 50 degrees C, and the range whose depth of discharge is 30 - 80%, input density is the range of 150 - 1300 W/kg, and power density is the range of 400 - 2800 W/kg, and is inferior also in input characteristics and output characteristics.

[0089] Moreover, in the case of the group cell which connected 96 of this cell to the serial, in the range whose temperature is -10 degrees C - 50 degrees C, and the range whose depth of discharge is 30 - 80%, input density is the range of 90-780W/kg, and power density is the range of 240 - 1680 W/kg, and is inferior also in input characteristics and output characteristics.

[0090] [Example 8] The charge-and-discharge effectiveness other than an above-mentioned effect is about 100%, and the lithium rechargeable battery which used the multiple oxide of this invention for the positive electrode has the feature with the good reversibility of insertion and emission of Li.

[0091] The partial cross section of the lithium rechargeable battery of this invention is shown in drawing 8 . The laminating of a negative electrode 2 and the positive electrode 3 was carried-out through the separator 1 of fine porosity polypropylene nature, this was wound spirally, and it inserted in the cell can 4 made from SUS.

[0092] The negative electrode 2 is connected to the cell can 4 through negative-electrode lead-wire 2a. The positive electrode 3 is connected to the lid 4 of a metal member through positive-electrode lead-wire 3a. The inside of the cell can 4 is made airtight through the insulating section 5 a lid 4, the cell can 4, and in between. The electrolytic solution was poured in in the cell can 4. Moreover, about the positive-electrode terminal 6, a height and the pars basilaris ossis occipitalis of the cell can 4 of the opposite side are the negative-electrode terminals 7 again at the height of a lid 4.

[0093] As shown in \*\* type explanatory drawing of drawing 9 , the negative electrode 2 provides carbon layer 2C in charge collector 2B. The positive electrode 3 has prepared multiple oxide layer 3C which contains Li and Mn of this invention in charge collector 3B. If current is passed among two poles, Li ion can move from multiple oxide layer 3C that there is no failure in carbon layer 2C in any way.

[0094] The \*\* type perspective diagram showing the crystalline structure of a multiple oxide layer explains this reason to drawing 10 . Multiple oxide layer 3C consists of two or more regular crystal-lattice 3D. When Li ion emits from crystal-lattice 3D, it is spread in carbon layer 2C like drawing 12 and drawing 13 more promptly [ defective 3F, transition 3G, etc. / since there are few with which it is interfered ] than the conventional technology mentioned later.

[0095] On the other hand, in the conventional crystal-lattice 3D of drawing 11 , when Li ion emits, it will be interfered by variant-part part 3E lacking in the regularity of a crystal, it becomes impossible to move to carbon layer 2C, and discharge effectiveness will fall. It is also the same as when Li ion inserts in multiple oxide layer 3C from carbon layer 2C on the contrary.

[0096] Thus, the lithium rechargeable battery which used multiple oxide layer 3C containing Li and Mn of this invention has the good reversibility of insertion and emission of Li, and it can maintain it about 100% in charge-and-discharge effectiveness.

[0097] [Example 9] The cell was produced like the example 1. About other conditions, it considered as optimal within the limits which this invention specifies. About negative-electrode discharge capacity, the capacity of a negative-electrode single electrode was evaluated by making Li metal into a counter electrode. Relation with the cycle life and negative-electrode discharge capacity to the negative-electrode true density of negative-electrode carbon is shown in drawing 14. From drawing, rather than 1.8 g/cm<sup>3</sup>, negative-electrode true density is a small larger range than 1.2 g/cm<sup>3</sup>, and showed the property also with a good cycle-life and negative-electrode discharge capacity.

[0098] Furthermore, in the cell, in the range whose temperature is -10 degrees C - 50 degrees C, and the range whose depth of discharge is 30 - 80%, input density was in the range of 300-1800W/kg, and power density was in the range of 500 - 3500 W/kg.

[0099] Moreover, in the case of the group cell which connected 96 of this cell to the serial, in the range whose temperature is -10 degrees C - 50 degrees C, and the range whose depth of discharge is 30 - 80%, input density was in the range of 200 - 1300 W/kg, and power density was in the range of 360 - 2520 W/kg.

[0100] [Example 10] It is \*\*\*\*\* about a cell like an example 1. About other conditions, it considered as optimal within the limits which this invention specifies. The relation between the crystal thickness Lc of negative-electrode carbon, input density, and power density was evaluated. The crystal thickness Lc of negative-electrode carbon showed the property with good input density and power density in the range of 5-150A, in the cell, it is the range whose temperature is -10 degrees C - 50 degrees C, and the range whose depth of discharge is 30 - 80%, input density had it in the range of 1000 - 1800 W/kg, and power density had it in the range of 2500 - 3500 W/kg.

[0101] Moreover, in the case of the group cell which connected 96 of this cell to the serial, in the range whose temperature is -10 degrees C - 50 degrees C, and the range whose depth of discharge is 30 - 80%, input density was in the range of 800 - 1300 W/kg, and power density was in the range of 2000 - 2520 W/kg.

[0102]

[Effect of the Invention] According to this invention, the long lasting lithium rechargeable battery was able to be obtained by using the long lasting material of this invention under a 50-degree C elevated temperature. Moreover, the lithium rechargeable battery which used the multiple oxide containing Li and Mn of this invention can supply power promptly corresponding to fluctuation of a load.

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[Translation done.]